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Evaluation and Auger Analysis of a Zinc-Dialkyl-Dithiophosphate Antiwear Additive in Several Diester Lubricants

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SUMMARY

The wear of pure iron in sliding contact with hardened M-2 tool steel was measured for a series of synthetic diester fluids, both with and without a zinc-dialkyl-dithiophosphate (ZDP) antiwear additive, as test lubricants. Selected wear scars were analyzed by an Auger emission spectroscopy (AES) depth-profiling technique to assess the surface-film elemental composition. The ZDP was an effective antiwear additive for all the diesters except dibutyl oxalate and dibutyl sebacate. The high wear measured for the additive-containing oxalate was related to corrosion; the higher wear measured for the additive-containing sebacate was due to an oxygen interaction. The AES of dibutyl sebacate surfaces run in dry air and in dry nitrogen showed large differences only in the amount of oxygen present. The AES of worn surfaces where the additive was effective showed no zinc, only a little phosphorous, and large amounts of sulfur.

INTRODUCTION

Diesters have been used as synthetic lubricants since the 1940's. They have found widespread use primarily in the aircraft industry and more recently in the automotive industry as crankcase lubricants as that industry stresses improved fuel economy and alternative materials (refs. 1 and 2).

Most antiwear additive chemistry was originally developed for mineral oils, and attempts to use the same additives in synthetic fluids have not always been successful. In many cases the antiwear additives did not provide the same wear protection in the synthetic fluid as in the mineral oil. Generally, little analytical work has been performed to relate surface chemistry to additive performance in diesters.

This investigation attempts first to determine the effectiveness of a common antiwear additive (a zinc-dialkyl-dithiophosphate, ZDP) in several diester synthetic-lubricant base fluids and then to analyze the resultant surface chemistry with Auger emission spectroscopy (AES). Preliminary wear experiments were conducted on iron in various diesters with and without the ZDP additive. The respective wear rates were measured and used to screen those combinations that should be AES analyzed. A pin-on-disk configuration was used to evaluate lubricating performance. The diesters were diallyl adipate, dimethyl adipate, dipropyl adipate, dibutyl adipate, dibutyl sebacate, dibutyl oxalate, and dibutyl succinate. The specific ZDP additive was zinc-o-o'-di-n-pentylphosphorodithioate.

APPARATUS AND PROCEDURE

Wear Measurements

The wear experiments were conducted with a multiple-pin-on-disk device that is commonly used in friction and wear studies (fig. 1). The disks were hardened M-2 tool steel (61 Rockwell C) circumferentially ground to 4 to 8 rms with a diameter of 6.3 centimeters. The pins were hemispherically tipped pure (99.99 percent) annealed iron with a radius of 0.476 centimeter. The disk was mounted on a shaft driven by a slow-speed electric motor. The pin was loaded normal to the surface of the rotating disk. Loading was achieved by hanging weights on the rider holder arm. The same sliding speed of 2.5 centimeters per second and the same load of 4.9 newtons (500 gf) were used for all experiments. These conditions provided data that correlated with full-scale automobile engine tests in previously unreported work. The entire apparatus was contained in a clear plastic box that could be continuously purged with dry air or dry nitrogen in order to control the ambient atmosphere.

For each experiment, newly prepared pin and disk specimens were used. Both the pin and the disk were rinsed with acetone and then scrubbed with a moist paste of 1-micrometer aluminum oxide polishing compound. After the scrubbing, the specimens were rinsed with water and ethyl alcohol and then dried. After the disk was mounted in the apparatus, the disk surface was covered with a thin layer of diester without any additive. A thin layer of lubricant was used rather than a lubricant reservoir so that equilibrium between the fluid and the atmosphere could be quickly obtained and the fluid would not need degassing. The plastic box was closed and purged before the experiment. An electric timer was used to stop the test at predetermined times so that the wear scar diameter could be measured. An impression of the wear scar diameter was made by inserting a piece of aluminum foil between the pin and the disk and then pressing the pin down. The scar diameter was then measured with a vernier-equipped microscope. In this manner, the pin and disk always were returned to the original contact position after the wear measurement.

After several readings over 40 hours insured that the wear rate was constant (linear by volume), the run was stopped and the diester fluid was replaced by fresh fluid containing 1 weight percent of ZDP. The run was then continued for 40 more hours to determine the wear rate with the additive present. After the run, the wear volume measurement was fitted by a least-squares method to a linear function of run time. The first 10 hours of a run were ignored to allow for the run-in of new specimens. This was necessary because wear rate measurements during various phases of the experiment had revealed that the higher wear rate during run-in is not representative of long-term wear behavior.

Auger Analysis

After the wear tests, the pins were rinsed in Freon solvent in order to remove the residual lubricant from the pin. The pins were then mounted in an ultra-high-vacuum system that attained a base pressure of 5×10^{-12} Pa (5×10^{-10} torr). The 25-micrometer-diameter electron beam for Auger analysis was aimed at the wear scar on a given pin by using a scanning sample positioner. The beam was then defocused to 0.1 millimeter diameter in order to guarantee that the elemental analysis of the surface was averaged over a sufficiently large area to be characteristic.

After alinement, each sample was depth profiled (i.e., argon ion beam sputtered along with AES analysis) in order to obtain its elemental composition as a function of depth. The ion sputtering was performed with a beam energy equal to 3000 electron volts at constant beam current with an argon pressure of 5×10^{-7} Pa (5×10^{-5} torr). The ion beam was continuously rastered over the entire wear scar surface in order to average the analysis. The electron beam had an energy of 2000 electron volts and a constant beam current of 50 nanoamperes. The low beam current was maintained to minimize beam damage to the surface.

RESULTS AND DISCUSSION

Wear Results

A typical plot of rider wear volume versus time in one of the diesters (diethyl adipate) is shown in figure 2. The linear wear rate in the pure diester was determined by a least-squares fit to be 1.0×10^{-5} cm^3/hr; that in the diester containing 1 weight percent of ZDP was determined to be 2.7×10^{-6} cm^3/hr. Thus the wear rate with the additive present was only 27 percent that for pure diester.

Not all diesters provided a decrease in wear rate when the additive was introduced. For example, a plot of rider wear volume versus time in dibutyl oxalate is shown in figure 3. With this fluid the wear rate increased from 1.3×10^{-5} cm^3/hr to 2.4×10^{-5} cm^3/hr, an 85-percent increase in wear rate with the additive. A bar chart summary of all the experiments is presented in figure 4.

The ZDP additive was effective in reducing the wear rate in all the adipate diesters. It was most effective in the diethyl and dipropyl adipates, where it reduced the rate to less than one-third that in the unformulated fluid. Although the additive reduced wear in the dibutyl adipate by over half, the wear rate was still more than twice that obtained in any other adipate.

In the dibutyl diesters, wear rates were lower with the additive in the adipate and succinate, but higher with the additive in the oxalate and sebecate. In particular, the

oxalate wear rate increased by 87 percent and the sebacate by 36 percent. Also shown in figure 4 are data for the dibutyl sebacate run in a dry nitrogen atmosphere. In this case, the wear rate in the fluid without any additive increased nearly four-fold over the dry-air value, yet showed a sharp drop with the additive. In order to better understand the wear results, AES examination of four selected wear scars was performed: The wear surface on the dibutyl oxalate showed a sharp increase in wear rate with the additive; the wear surface on the dibutyl adipate showed a reduction in wear rate with the additive; and the wear surface on the dibutyl sebacate showed significant differences with the additive in both dry air and dry nitrogen.

Auger Analysis of Wear Scars

A typical AES spectrum is shown in figure 5. The peak-to-peak heights on the curves are proportional to the quantity of element present. Comparisons can be made between surface compositions for the different lubricants. The comparisons are quantitative for the same element but not necessarily between elements. Although AES is primarily a technique for elemental analysis, some chemical information can be found from the peak shapes. For example, during sputtering the carbon peak changes from an amorphous graphite structure to a mixture of graphite and carbide to a carbide structure (fig. 6, ref. 3). Also, the low-energy iron peak located at 46 eV for clean iron shows some chemical structure. This peak is also shown in figure 6 at roughly the maximum in the film distributions, with the clean iron peak shown for comparison. The peak shapes suggest that the iron is in chemical combination with the other elements present (refs. 4 and 5), as might be expected. The complete elemental depth profiles for the four samples are shown in figures 7 to 10.

Although an absolute calibration of depth in terms of sputtering time was not obtained, the depths sputtered at corresponding times should be approximately the same because the materials were similar. The sputtering rate was estimated by sputtering a 100-nanometer (1000-Å) tantalum oxide film under the same conditions. The rate obtained was 1.8 nanometers per minute (18 Å/min). This value cannot be verified, but it may be correct to a factor of 2 or 3, judging from typical variations of sputtering yields. A secondary consideration is that in sputtering rough surfaces such as wear scars, pitted regions occur in between fairly uniform regions. Thus, in depth profiling, although the uniform regions of the film are removed rapidly, the pitted regions remain essentially unchanged. This leads to broadening in the elemental distributions as a function of depth. Only the regions where rapid changes have occurred have been plotted. These regions are representative of the uniform, high-contact-area regions, where chemical reactions were evident. However, long-term sputtering was performed on all samples.

These depth profile results have some interesting features. The dibutyl adipate and dibutyl sebacate lubricated riders (figs. 7 and 8) run in air had similar qualitative surface compositions; both had a region of surface film containing carbon that changed from amorphous carbon to a mixture of amorphous carbon, carbide, oxygen, and sulfur. Very little phosphorous was detected in either case (not plotted) and no zinc.

The film on the iron rider lubricated with dibutyl sebacate was somewhat thicker and contained considerably larger amounts of both oxygen and sulfur. This is surprising in view of the wear results, in which the adipate sample showed a reduction in wear rate with ZDP and the sebacate showed an increase. The Auger analysis did not reveal, however, the chemical compounds of the oxygen and/or sulfur present. It may be that on the sebacate sample run in dry air the sulfur was in combination as a sulfate rather than as a metal sulfide. This is a likely possibility in view of the depth profile of the dibutyl sebacate lubricated riders run in a nitrogen atmosphere with ZDP (fig. 9). In this profile, the oxygen level is low, yet the sulfur concentration is still very high. In this case the wear rate was markedly lower than that for the sebacate run in air.

Oxygen is known to affect the decomposition of ZDP (ref. 6). Decomposition is thought to be a precurser of film formation (ref. 7), and the type of decomposition product can certainly affect the type of reaction product that can or will occur during film formation. Conclusive evidence, however, concerning the chemical compounds present will require analysis by X-ray photoelectron spectroscopy or a similar technique.

The dibutyl oxalate depth profile (fig. 10) shows a very thin film containing no detectable phosphorous and only a relatively small amount of sulfur. The balance of the film is amorphous carbon, oxygen, and iron. The iron Auger peak is shaped as if an oxide rather than a carbide or a sulfide were present (ref. 4). It is likely that the very acidic nature of the dibasic acid from which this diester is formulated (oxalic acid, ionization constant $K_1 = 5.7 \times 10^{-2}$ (ref. 8)) promotes corrosion of the iron. This is clearly reflected in the high wear rate with the unformulated diester fluid.

Since most antiwear additives are themselves corrosive to some extent, adding ZDP will probably increase the wear rate when the base fluid is corrosive. This hypothesis is supported by the observation of a heavy crust built up on the sides of the wear scar. It has also been reported in the literature that the decomposition of ZDP can be catalyzed by an acidic environment (ref. 6).

SUMMARY OF RESULTS

Wear experiments and Auger emission spectroscopy of pure iron sliding against M-2 tool steel lubricated with diesters containing a ZDP (zinc-o-o'-di-n-pentylphosphorodithioate) antiwear additive were performed. The following results were obtained:

1. The ZDP additive successfully reduced the wear rate for the entire series of adipate diesters examined (diallyl, dimethyl, diethyl, dipropyl, and dibutyl).

2. For a series of diesters based on the same functional alcohol-derived group (-dibutyl-), ZDP was not effective in reducing wear in dry air. With dibutyl oxalate and dibutyl sebacate lubricated riders run in dry air, the wear rate increased with the addition of ZDP. However, with dibutyl sebacate run in dry nitrogen, the wear rate decreased with the addition of ZDP.

3. Auger analysis of worn surfaces showed little qualitative difference between the elemental compositions of surface films on the iron pins run with ZDP in dibutyl adipate (lower wear rate) and in dibutyl sebacate (higher wear rate). In general the surfaces contained oxygen, sulfur, and carbon with little phosphorous and no zinc.

4. Auger depth profiles of wear scars on iron riders lubricated by ZDP-containing dibutyl sebacate and tested in dry nitrogen showed that the films contained about the same amount of sulfur but not much less oxygen than did samples tested in dry air.

5. Auger depth profiles of wear scars on iron riders lubricated by ZDP-containing dibutyl oxalate showed that the very thin films contained mostly carbon and oxygen and some sulfur. Excessive corrosion by both lubricant and additive are believed to occur with this combination.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 15, 1979,
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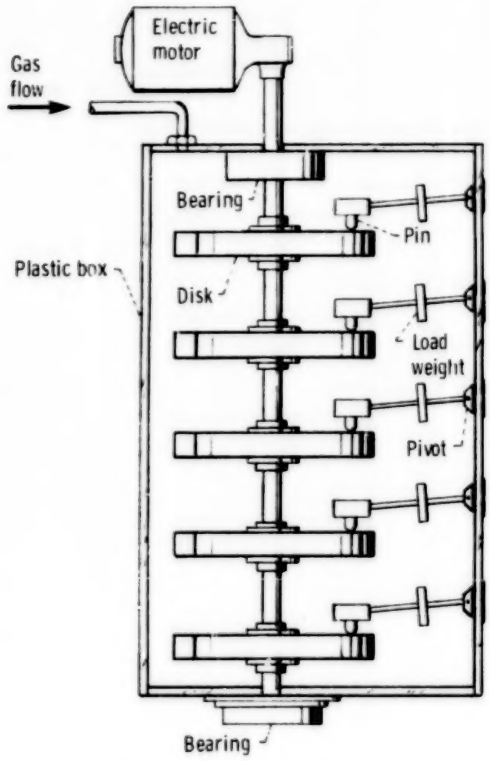


Figure 1. - Multiple-pin-on-disk wear testing apparatus.

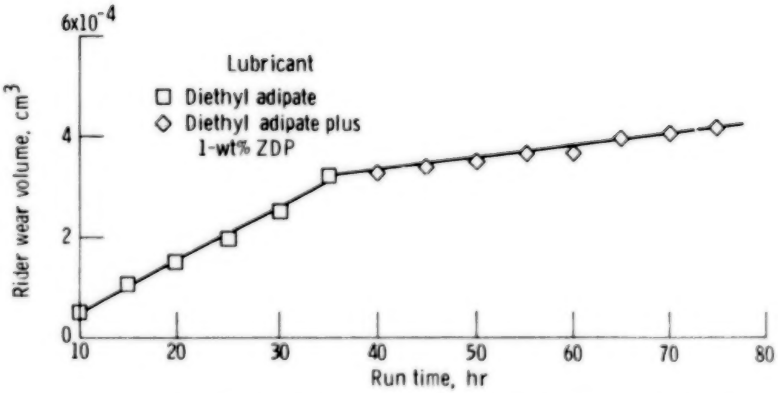


Figure 2. - Wear volume as function of time for pure iron sliding on M-2 tool steel. Sliding velocity, 2.5 cm/sec; load, 4.9 newtons; atmosphere, dry air; lubricant, diethyl adipate.

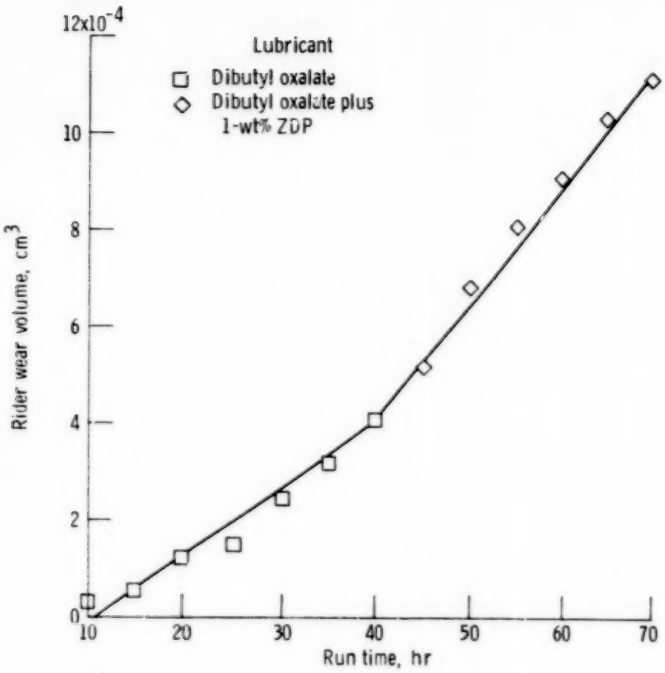


Figure 3. - Wear volume as function of time for pure iron sliding on M-2 tool steel. Sliding speed, 2.5 cm/sec; load, 4.9 newtons; atmosphere, dry air; lubricant, dibutyl oxalate.

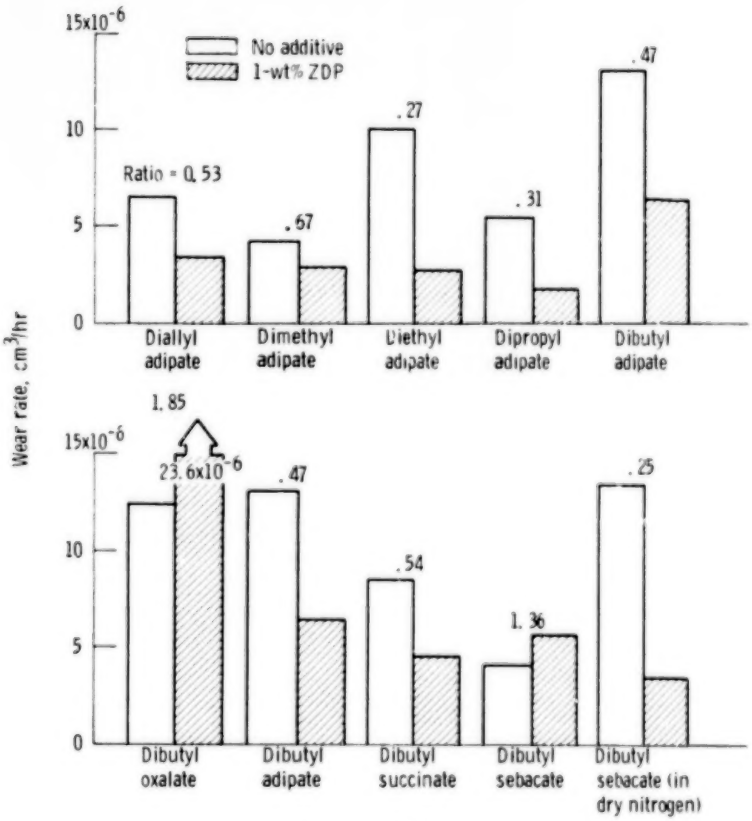


Figure 4. - Wear rates of pure iron sliding on M-2 tool steel in various diesters with and without ZDP antiwear additive. Sliding speed, 2.5 cm/sec; load, 4.9 newtons; atmosphere, dry air, except where noted as dry nitrogen.

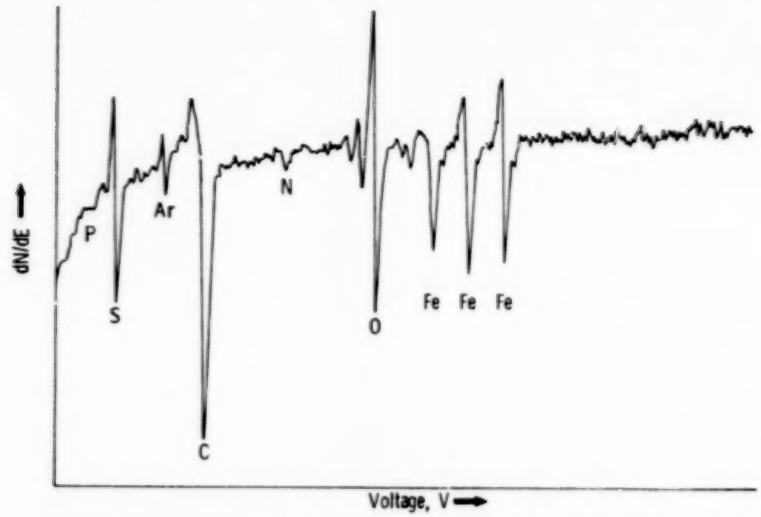
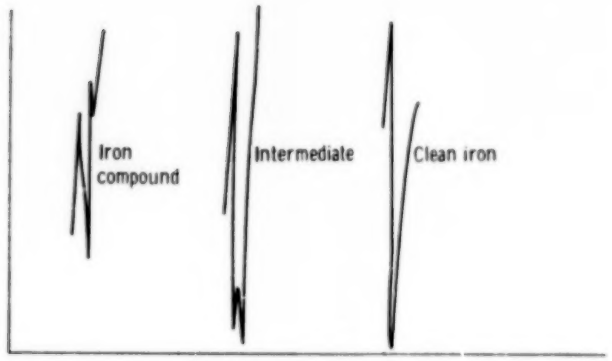
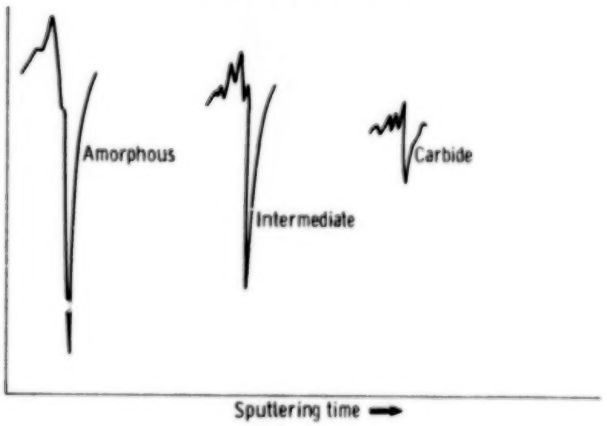


Figure 5. - Auger spectrum of wear scar on pure iron pin run against M-2 tool steel disk in dibutyl adipate containing 1-wt% ZDP. Sliding speed, 2.5 cm/sec; load, 4.9 newtons; atmosphere, dry air.



(a) 46-eV iron peak shape.



(b) Carbon peak shape.

Figure 6. - Variation in Auger carbon and iron peak shapes with sputtering time.

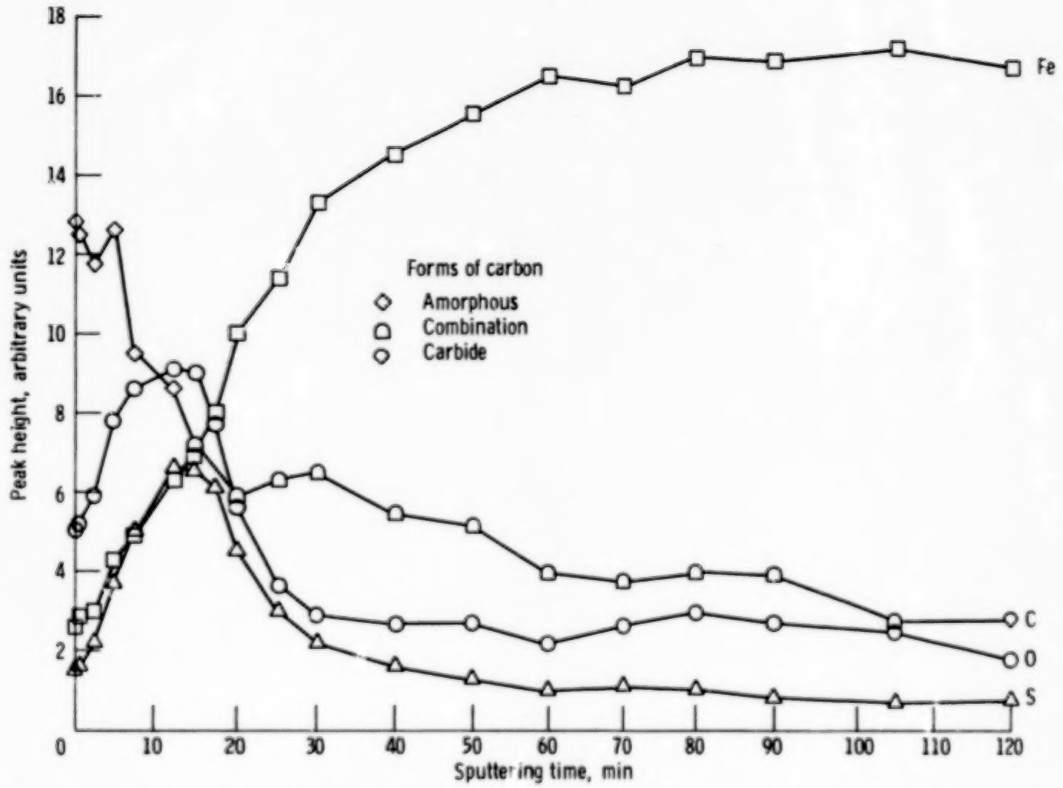


Figure 7. - Elemental depth profile of wear scar on iron pin run in dibutyl adipate plus 1-wt% ZDP. Sliding speed, 2.5 cm/sec; load, 4.9 newtons; atmosphere, dry air.

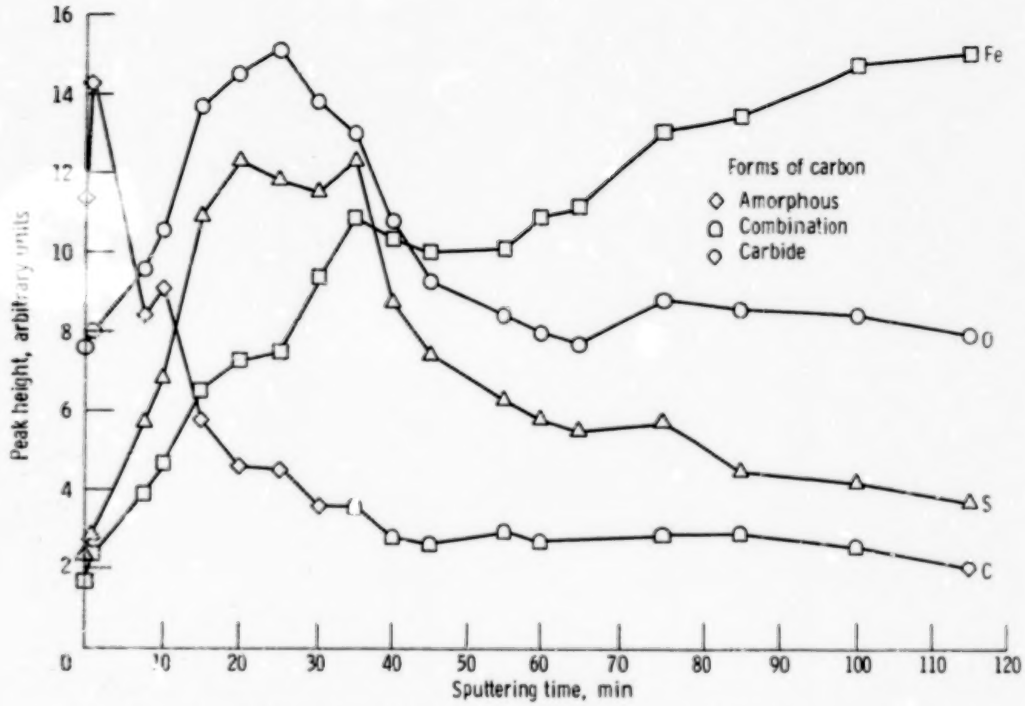


Figure 8. - Elemental depth profile of wear scar on iron pin run in dibutyl sebacate plus 1-wt% ZDP. Sliding speed, 2.5 m/sec; load, 4.9 newtons; atmosphere, dry air.

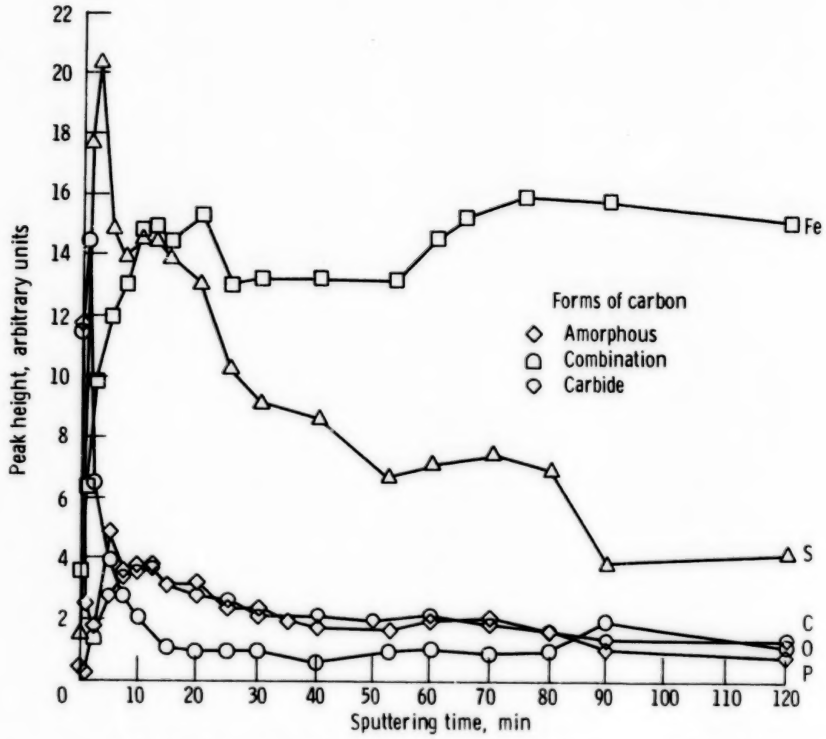


Figure 9. - Elemental depth profile of wear scar on iron pin run in dibutyl sebacate plus 1-wt% ZDP. Sliding speed, 2.5 cm/sec; load, 4.9 newtons; atmosphere, dry nitrogen.

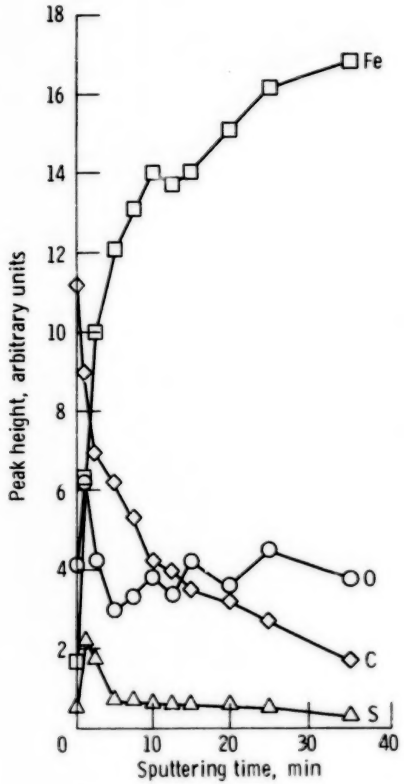


Figure 10. - Elemental depth profile of wear scar on iron pin run in dibutyl oxalate plus 1-wt% ZDP. Sliding speed, 2.5 cm/sec; load, 4.9 newtons; atmosphere, dry air.

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15. Supplementary Notes

16. Abstract

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